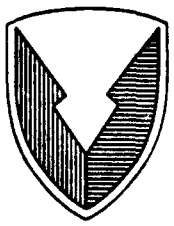

Research and Development Technical Report
SLCET-TR-92-12

Processing and Characterization of Electrophoretically Deposited Holmium Barium Copper Oxide Superconductor Films

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September 1992

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	September 1992	Technical Report: 1991

4. TITLE AND SUBTITLE
PROCESSING AND CHARACTERIZATION OF ELECTROPHORETICALLY DEPOSITED HOLMIUM BARIUM COPPER OXIDE SUPERCONDUCTOR FILMS

5. FUNDING NUMBERS
PE: 060110
PR: 1L161102AH47
TA: 01
WU: 04 DA302913

6. AUTHOR(S)
Michelle A. Dornath-Mohr, Donald W. Eckart, Robert D. Finnegan, Ernest Potenziani II, William Wilber; and Arthur Tauber (Geo-Centers, Inc.)

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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Electronics Technology and Devices Laboratory (ETDL)
ATTN: SLCET-ET
Fort Monmouth, NJ 07703-5601

8. PERFORMING ORGANIZATION REPORT NUMBER
SLCET-TR-92-12

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT
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12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Thick films of $HoBa_2Cu_3O_{7-x}$ (HBCO) were electrophoretically deposited on bulk $YBa_2Cu_3O_{7-x}$ (YBCO) pellets in magnetic fields of 0 and 2 T. X-ray diffraction patterns indicated no preferred orientation for the films. Scanning electron microscopy revealed that the films averaged 7 microns thick, have an open pore structure with microbridges between particles, and a minimal amount of grain growth. Some microcracking of the films was observed. The surface resistivities (R_s) of the films were measured from 5 to 140K using a resonant cavity at 35 GHz. The best films had a R_s of 30 milliohms at 10K. The transition temperature (T_c) of the films ranged from 85 to 90K as measured by the four-point probe method.

14. SUBJECT TERMS
Superconductors; Ceramics; Microwaves; Processing Thick Films

15. NUMBER OF PAGES
15

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL

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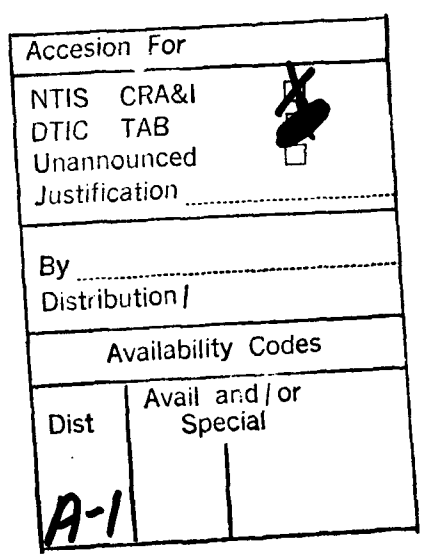

FIGURES

INTRODUCTION

High temperature superconductors have been investigated for many potential applications. The rf properties of the best thick films[1-4] are clearly not comparable to thin films made by various methods.[5] However, several applications require large area coverage and continuous, low cost fabrication. In these cases, thick films, despite their poorer electrical properties, could be a good compromise between high performance and technical applicability.

Thick films of high temperature superconductors have been prepared by various methods including screen printing,[6] spinning,[7] sol-gel,[8] plasma spraying,[9] spray pyrolysis,[10] and electrophoretic deposition.[1-4, 11-14] The advantages of electrophoretic deposition include the ability to produce uniform films over irregularly shaped substrates,[4, 14] and adaptability to large area, continuous fabrication. Also, highly oriented[1] and strongly adherent films are possible. The deposition time is short and the set-up is simple and inexpensive.

Electrophoretic deposition is a promising technique for large scale and electronic device applications. Applications include cavities for particle accelerators, magnetic shields, large area microwave devices such as antennas and filters, high Q cavities, and Superconducting Magnetic Energy Storage (SMES). These applications require layers, a few microns in thickness, deposited on suitable and mechanically rigid substrates.

The high T_c oxide superconductors have anisotropic transport properties, therefore alignment of the grains is necessary for good rf behavior.[15, 16] One method of grain alignment is to deposit the film in a magnetic field.[2] Because Holmium (Ho) has a larger magnetic moment than Yttrium (Y), substitution of Y with Ho should result in greater alignment of grains with the same magnetic field. $HoBa_2Cu_3O_{7-x}$ (HBCO) has essentially the same T_c as $YBa_2Cu_3O_{7-x}$ (YBCO).[17]

EXPERIMENTAL

The HBCO powder was synthesized using the nitrate method. The appropriate amounts of Ho_2O_3, CuO, and $BaCO_3$ were weighed out, mixed, and dried. The dried powders were placed on a porcelain casserole and enough HNO_3 50% by volume was added to wet the mixed powder. After this reaction, the mixture was allowed to slowly evaporate until dry. The solidified nitrate cake was placed in a tube furnace and heated to 600°C in

an inert atmosphere to decompose the mixture to an oxide. The mixture was allowed to cool to room temperature, ground to a powder, pressed into thin pellets, and sintered at 850°C for 10 to 24 hrs., in air or flowing O_2. The pellets were ground again to approximately 100 micron particle size, pressed into thin pellets and resintered by the following schedule:

room temperature to 930°C	7 hrs.
soak at 930°C	20 hrs.
930°C to 650°C	4 hrs.
soak at 650°C	10 hrs.
650°C to 450°C	2 hrs.
soak at 450°C	10 hrs.

The sintered pellets were reground to approximately 100 micron particle size and then jet milled to 2 micron average particle size.

A suspension was produced by mixing 3 g of HBCO powder with 25 cc of an organic carrier. Three different carriers were tested: ethanol, methanol, and acetone, with acetone yielding the best results. The mixture was vigorously shaken just prior to deposition to insure that the particles were well dispersed.

The substrates used were metallic YBCO pellets, ground flat and polished. During the electrophoretic deposition process, the substrate acts as one of the electrodes and therefore must be conducting. Metallic YBCO pellets are conducting and should reduce contamination of the film by the substrate during processing. Some of the pellets contained trace amounts of elemental Ag.

The electrophoresis apparatus (see figure 1) consists of a Kel-F cell into which the suspension is placed. Two electrodes, one of which is the substrate, are attached to the cap of the cell. The applied voltage is 450 to 1000 V/cm with a current range of several microamps to 3 mA. Figure 2 shows a schematic of the electrophoretic set-up. The length of deposition ranged from 3 to 10 mins. and was performed in magnetic fields of 0 and 2T fields.

Following electrophoretic deposition the films were dried for 1 hr. at 120°C in air. The films were sintered for 30 mins. in the hot zone of a furnace preheated to 920°C. They were then pulled into the cool zone and the hot zone was cooled to 450°C. The films were returned to the hot zone for 2 hrs. and then allowed to furnace cool. Sintering and annealing were done in flowing O_2.

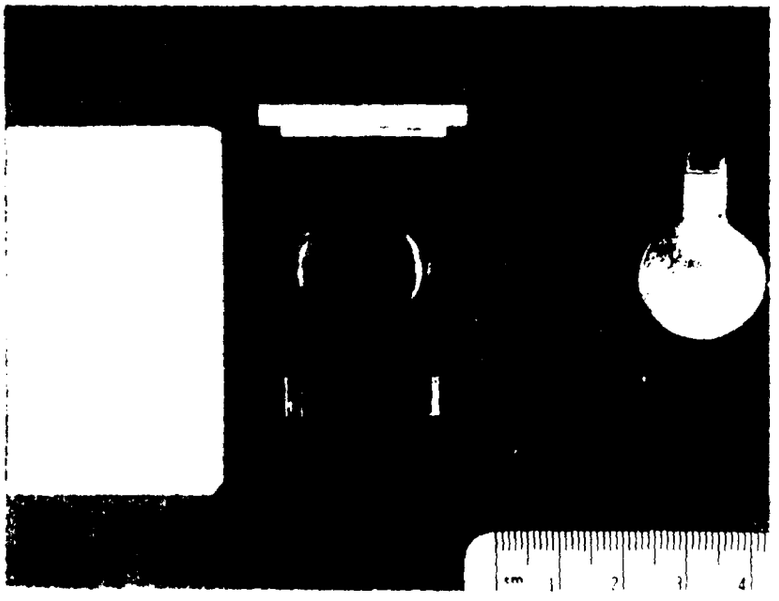

Figure 1. Electrophoretic apparatus consisting of a Kel-F cell and two electrodes.

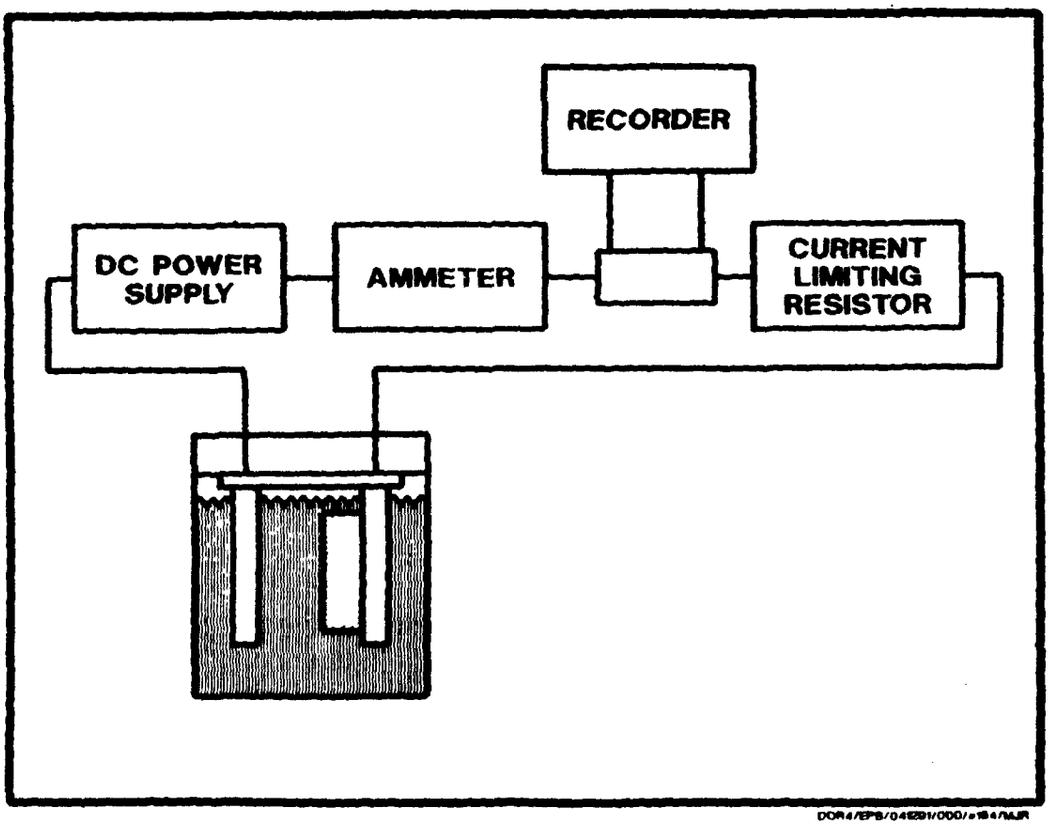

Figure 2. Schematic of electrophoretic set-up.

RESULTS AND DISCUSSION

X-ray diffraction shows no orientation of the c-axis for any of the films, regardless of deposition conditions. Generally, the patterns were single phase but occasionally $BaCO_3$ and the 211 phase were found.

Energy Dispersive Analytical X-ray (EDAX) shows that small amounts of Y and Ag, when present in the substrate, diffused into the films. Although there is some evidence[18] that Ag increases the R_s of bulk YBCO, comparison of HBCO films with and without Ag and Y showed no indication of Ag or Y having any significant effects on the films. The effect of Ag on HBCO thick films was not thoroughly investigated at this time.

The Scanning Electron Microscope (SEM) micrograph in figure 3 shows a typical surface of the sintered films with grain size ranging from 2 to 4 microns. The surface is porous with microbridges between particles and a minimal amount of grain growth. There is evidence of incongruent melting of the grains. Microcracking was observed in several of the films. The thickness of the films was measured by SEM to be approximately 7 microns.

Figure 3. SEM micrograph showing a typical surface of the sintered HBCO films with grain size ranging from 2 to 4 microns.

Because the films are porous there was concern that the YBCO pellets were being measured rather that the HBCO thick films. To insure this was not the case, the YBCO pellets were characterized prior to film deposition. The YBCO pellets had high R_s (0.2 ohms) and in general were very poor superconductors. Even following regenerative heat treatment, the YBCO pellets remained poor superconductors.

The rf properties of the films were measured in the microwave field of a copper cavity excited in the TE_{011} mode at 35 GHz. The sample acted as an end plate of the cavity which has a diameter of 0.75 inch as shown in figure 4. The R_s of the films was determined from the change in the unloaded Q of the cavity upon insertion of the sample through a temperature range of 5 to 140K. The surface resistances of the best films was 0.031 ohms at 10K as shown in figure 5. A T_c of 87K was measured for this film by four-point probe as shown in figure 6. The experimental R_s of copper at 10K is 0.0228 ohms. The R_s of the other films ranged from 0.06 to 0.73 ohms with transitions falling between 85 and 90K. Some films did not show any superconductive behavior, which is believed to be due to microcracking and peeling of the film.

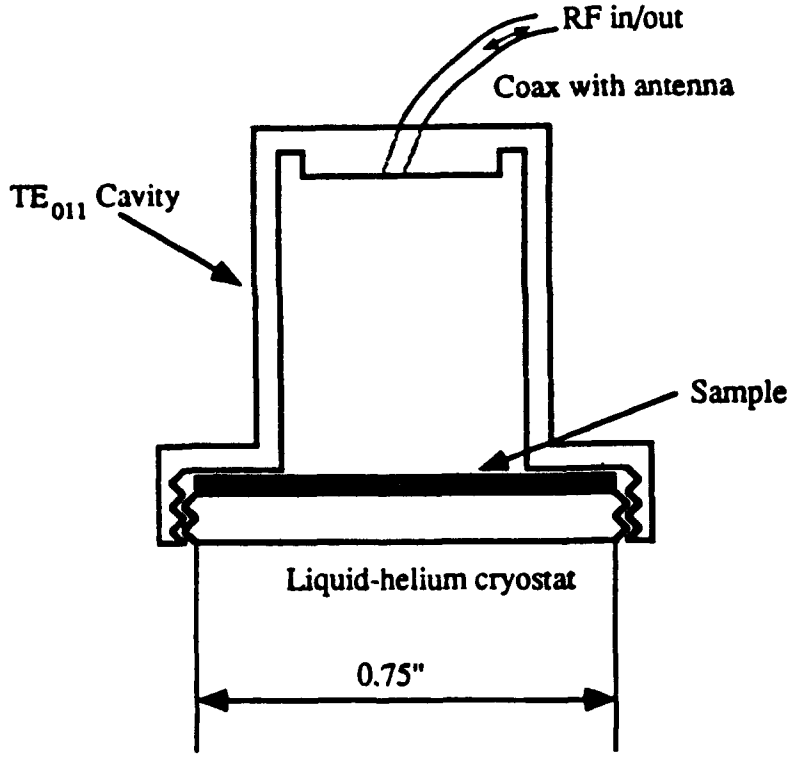

Figure 4. Diagram of copper cavity used for R_s measurements.

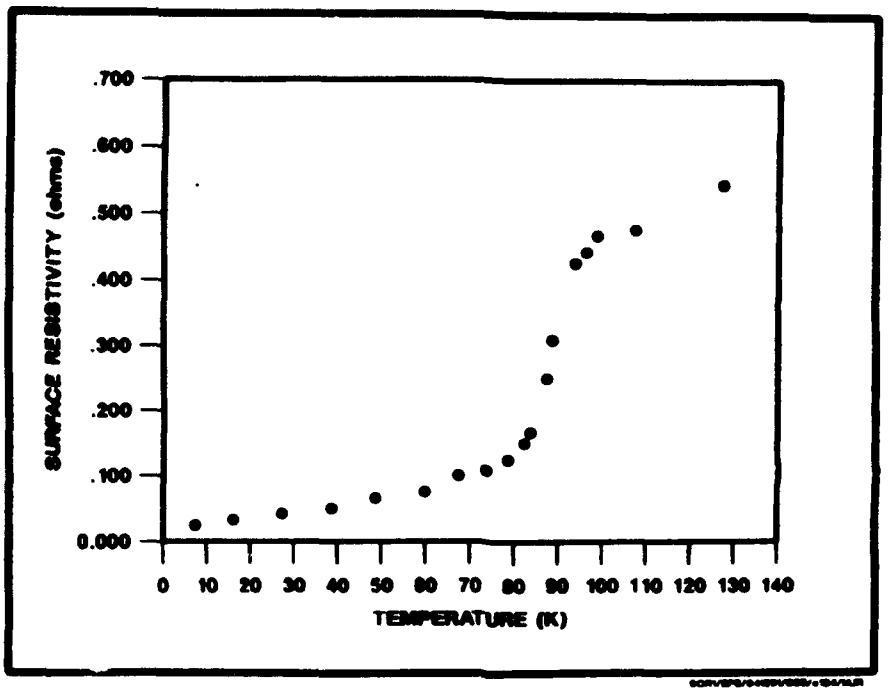

Figure 5. R_s vs temperature of a typical HBCO film..

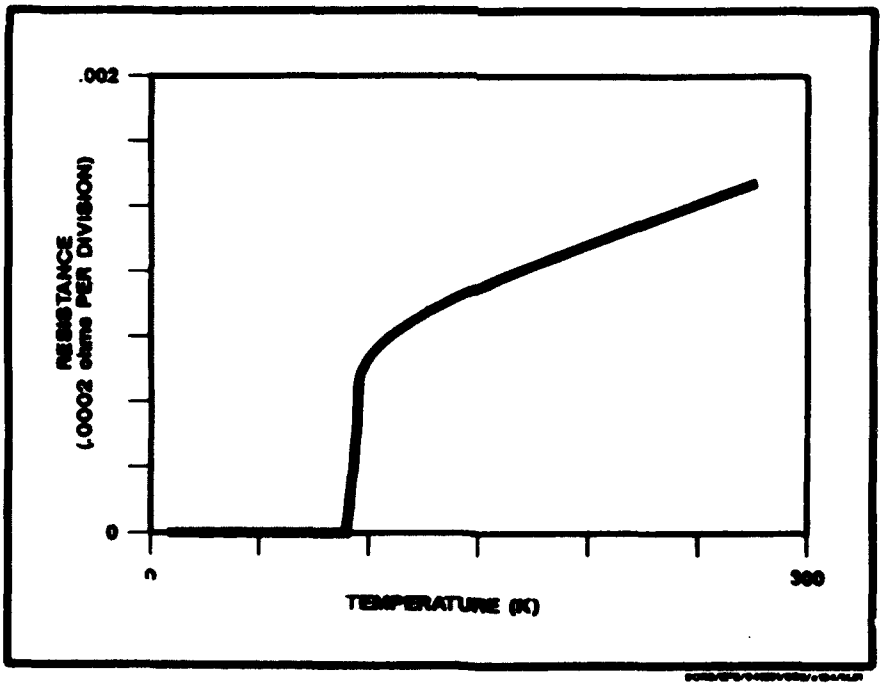

Figure 6. Four-point probe measurements of a typical HBCO film.

CONCLUSIONS

Electrophoretic deposition of HBCO thick films on metallic YBCO pellets has produced uniform films with sharp transitions and low surface resistances. The simplicity and low cost of the method as well as its potential for textured, conformal coatings makes it a promising option for many applications.

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